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(54) GELATINIZING AGENT OR SOLIDIFYING AGENT FOR ORGANIC LIQUID

(57)Abstract:

PURPOSE: To obtain a gelatinizing agent or solidifying agent useful as a solvent, a treating agent for an oil agent, a lubricant, a mold release agent, an adhesive, a binder, a sealing agent, etc., capable of forming a uniform, smooth, viscous and stable gelatinized or solidified material by adding a small amount of the gelatinizing agent or solidifying agent to an ester, fats and oils, a hydrocarbon, a polar or nonpolar organic solvent, etc., liquid at a normal temperature.

CONSTITUTION: This gelatinizing agent or solidifying agent for an organic liquid (with the proviso that a ≥ 4 C monohydric alcohol in the case in which the organic liquid is an alcohol) comprises an esterification product of glycerol or its condensed substance, a 2-28C straight-chain saturated fatty acid and a 12-28C aliphatic saturated dibasic acid.

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CLAIMS

[Claim(s)]

[Claim 1] Gelation or the solidification agent of the organic liquid (with a carbon numbers of four or more monohydric alcohol when [however,] an organic liquid is alcohol) which consists of an esterification product of a glycerol or its condensate, the straight chain-like saturated fatty acid of carbon numbers 2-28, and the aliphatic series saturation dibasic acid of carbon numbers 12-28.

[Claim 2] The gelation according to claim 1 or the solidification agent whose carbon numbers of straight chain-like saturated fatty acid are 22-28 when the carbon number of an aliphatic series saturation dibasic acid is less than 20.

[Claim 3] The gelation according to claim 1 or the solidification agent whose carbon numbers of straight chain-like saturated fatty acid are 18-28 when the carbon number of an aliphatic series saturation dibasic acid is 20.

[Claim 4] The gelation according to claim 1 or the solidification agent whose carbon numbers of straight chain-like saturated fatty acid are 2-28 when the carbon number of an aliphatic series saturation dibasic acid is 28.

[Claim 5] The gelation according to claim 1, 2, 3, or 4 or the solidification agent which is the alcohol with which an organic liquid (with a carbon numbers of four or more monohydric alcohol when [however,] an organic liquid is alcohol) presents the shape of liquid in ordinary temperature, a fatty acid, ester, the ether, or a hydrocarbon.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the esterification product which gels or solidifies a liquefied organic liquid (with a carbon numbers of four or more monohydric alcohol when [however,] an organic liquid is alcohol) in ordinary temperature. Gelation or the solidification agent of this invention can be used in the processing fields, such as the electrical and electric equipment, an electron, the device for MAG, a machine, an automobile, the miscellaneous goods for days, a color, ink, a coating, cosmetics, toiletries, drugs, agriculture, fishery, feed, the food field and paper, fiber, leather, resin, a macromolecule, rubber, and a metal, etc.

[0002]

[Description of the Prior Art] Conventionally, the metal soap of (1) higher fatty acid, 12-hydroxy stearin acid, a JIBEN zylidene sorbitol, JIBEN zylidene xylitol, a N-acylamino acid derivative, (2) dextrin fatty acid ester, an acrylic-acid system polymer, etc. are known as what has the function which solidifies fats and oils, a hydrocarbon, or a solvent to gel.

[0003] Among these, the type of (1) solidifies the whole to gel by making it dissolve or distribute in liquefied ester and fats and oils, and mainly cooling to homogeneity, at them. this gelling agent -- melting point [of 12-hydroxy stearin acid]: -- 80 degrees C and melting point: 160 degree C of a JIBEN zylidene sorbitol -- as -- generally, the melting point was high, and in solidifying the so-called organic liquefied objects, such as fats and oils, for this reason, it needed to perform heating actuation beforehand, and to dissolve the gelling agent itself, or to carry out melting of for example, a gelling agent and the fats and oils. Moreover, to organic solvents, such as general-purpose isoparaffin, a hexane, and a butanol, it dissolved industrially as a solvent of a low-boiling point, and it begins by adding very a lot of gelling agents, and can solidify, and this type of gelling agent was unsuitable to solidification of this organic solvent.

[0004] On the other hand, although there is "an AKUA rucksack CA" by Nippon Shokubai Kagaku Kogyo Co., Ltd., for example as an acrylic-acid system polymer as a gelling agent of the type of (2) and this solidifies almost all the hydrocarbons system compound, to the fats and oils which have an ester system compound and alkyl group chain length's large higher-fatty-acid residue, there is especially no **** about the effectiveness of gel solidification. And this type of thing was difficult for obtaining a uniform gel object, in order to make the so-called gelled object absorb in a gelling agent and to solidify to the things of the aforementioned (1) type being melting and a thing to solidify about a gelling agent and a gelled object.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is little addition about organic liquids, such as alcohols (however, with a carbon numbers of four or more monohydric alcohol) which present the shape of liquid in ordinary temperature, ester, and hydrocarbons, and is to offer homogeneity and a smooth solid-state-like object, a gel solidification object and the gelation to make, or a solidification agent preferably.

[0006]

[Means for Solving the Problem] In order to attain said purpose, this invention persons came to complete a header and this invention for a gel object or a solidification object being obtained by using a specific esterification product, as a result of repeating examination wholeheartedly. That is, this invention is gelation or the solidification agent of the organic liquid (with a carbon numbers of four or more monohydric alcohol when [however,] an organic liquid is alcohol) which consists of an esterification product of a glycerol or its condensate (henceforth a glycerol etc.), the straight chain-like saturated fatty acid (only henceforth a fatty acid) of carbon numbers 2-28, and the aliphatic series saturation dibasic acid (only henceforth a dibasic acid) of carbon numbers 12-28.

[0007] As an indispensable raw material component for manufacturing the esterification product of this invention, there is a glycerol etc. first. Among these, average degree of polymerization is polyglycerin of 2-10 preferably two or more, and a glycerol condensate can illustrate diglycerol, triglycerol, a tetra-glycerol, a hexa glycerol, a deca glycerol, etc., and can use these as mixture including independent or a glycerol.

[0008] Next, a fatty acid, i.e., a monobasic acid, makes it indispensable for a carbon number to be the straight chain-like saturated fatty acid of 2-28. An acetic acid, a propionic acid, a caproic acid, a caprylic acid, a capric acid, a lauric acid, a myristic acid, a palmitic acid, stearin acid, 10-hydroxy stearin acid, 10-keto stearin acid, 12-hydroxy stearin acid, arachin acid, a HEBEN acid, a montanoic acid, etc. can be raised as an example as concrete straight chain-like saturated fatty acid, and in this invention, even if it uses these with independent or mixture, it does not interfere.

[0009] Moreover, as a dibasic acid, a carbon number needs that it is the thing of the letter of aliphatic series saturation of 12-28. The thing or carbon number of partial saturation cannot obtain easily the dibasic acid to which, as for the esterification product of less than 12 dibasic acid, a carbon number exceeds 28 by gelation ability falling as a industrial raw material. therefore, independent [in dibasic acids such as dodeca dicarboxylic acid, tetra-deca dicarboxylic acid, eicosa dicarboxylic acid, a docosa KOSAJI carboxylic acid, tetracos a dicarboxylic acid hexacos a dicarboxylic acid, and OKUTAKOSA dicarboxylic acid,] in this invention -- or OKUTAKOSA dicarboxylic acid can be easily isolated from oil seeds including the Goma seed, and is [that what is necessary is just to use it, mixing] suitable.

[0010] Although the above mentioned fatty acid and the above mentioned dibasic acid can be used in this invention, combining them suitably, when the carbon number of a dibasic acid of especially desirable combination is less than 20, the carbon numbers of a fatty acid are 22-28, when the carbon number of a dibasic acid is 20, the carbon numbers of a fatty acid are 18-28, and when the carbon number of a dibasic acid is 28, the carbon numbers of a fatty acid are 2-28.

[0011] What is necessary is just to adopt either of the approaches described below, in order to obtain the esterification product of this invention using said raw material. that is, a glycerol etc. carries out the oligo esterification reaction of a fatty acid and the dibasic acid to coincidence, or a glycerol etc. and a fatty acid are esterified first -- making -- this -- further -- a dibasic acid and an oligo esterification reaction -- or an ester exchange reaction is carried out, or oligo esterification of a glycerol etc. and the dibasic acid is carried out first, and, subsequently the esterification reaction of this is carried out to a fatty acid.

[0012] Under existence of an acid, alkali, or a metal catalyst or nonexistence, in an organic solvent desirable and inactive for this reaction, or/and a gas, an esterification reaction removes the water which carries out a byproduction for several hours to 20 hours, and performs it at 100-240 degrees C. Moreover, an ester exchange reaction is performed at 20-140 degrees C for dozens of minutes to dozens hours using catalysts, such as a metal alcoholate or lipase. Said reactivity can be evaluated by measuring the presentation of the acid number in a system, or the acid component of a free state, and, thereby, should just determine the termination time of a reaction. Since a fatty acid and the fatty

acids which may contain a dibasic acid, in addition, carry out a byproduction, such as an unreacted glycerol, the glyceride of low molecular weight, etc. may be intermingled, esterification or an ester exchange reaction object will carry out separation removal of these by well-known approaches, such as rinsing and alkali deoxidation, if it requires, and if it requires further, decolorization and deodorization processing will be performed and it will refine them.

[0013] The esterification products of this invention obtained in this way are mixture with which oligo esterification of a fatty acid and the dibasic acid was carried out at the shape of the shape of a straight chain, and a mesh, such as a glycerol, and the melting point is about 50-80 degrees C. In addition, whenever [esterification / when using a glycerol condensate especially with high polymerization degree] does not necessarily need to be completeness (full ester), for example, should just have whenever [more than one half of these hydroxyl groups / esterification] with a deca glycerol from a PENTA glycerol. When whenever [esterification] is small, the gelation ability and solidification ability to the organic liquid made into the object of this invention are inferior. From the reaction mol equivalent of the reaction mol equivalent and fatty acids, such as the blending ratio of coal of a raw material, i.e., a glycerol etc., and a dibasic acid, the hydroxyl value of the esterification product of this invention can be computed easily, and can be adjusted. Moreover, it can adjust also by the existence of purification of reaction temperature, reaction time, and a reactant.

[0014] the esterification product of this invention is independent in this — or it can mix and can make with gelation or the solidification agent of an organic liquid. An organic liquid means the organic compound which presents a liquid in ordinary temperature here. A butanol, Ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, The butylene-glycol monoethyl ether, 2-ethylhexanol, Nonanol, 2-heptyl undeca Norian, 2-octyl dodecanol, With a carbon numbers [of the shape of the shape of a straight chain, such as oleyl alcohol, and a side chain, saturation, or partial saturation] of four or more monohydric alcohol Fatty acids, such as an acetic acid, a propionic acid, a caproic acid, a caprylic acid, oleic acid, and various isostearic acid Myristic-acid isopropyl, myristic-acid octyldodecyl, a Tori 2-ethyl hexanoic-acid glyceride, Ester, such as a mixed medium-chain-fatty-acid glyceride and ethyl acetate, soybean oil, oleum rapae, Sunflower oil, safflower oil, cotton seed oil, olive oil, sesame oil, the linseed oil, Hydrocarbons, such as ether, such as fats and oils, such as fish oil, and these partial decomposition products, wood ether, diethylether, and the petroleum ether, a pentane, a hexane, a heptane, an isooctane, paraffin, and isoparaffin, are suitable. In addition, it is hard to solidify by gelation or the solidification agent of this invention, and with a carbon number of three or less monohydric alcohol is not suitable as an object. Liquefied silicon oil, kerosene, etc. can be made into an object in the ordinary temperature other than these.

[0015] if it adds three to 5% of the weight and the esterification product of this invention is preferably required one to 10% of the weight to said organic liquid — about 80 degrees C — warming — after melting — light — stirring — ordinary temperature — **** — it is — if it cools and puts on about 5 degrees C gently, it will be uniform and a smooth gelation object or a smooth solidification object with viscosity nature thru/or a gel solidification object will be obtained. The whole system holds a homogeneity condition, without this thing generating a liquid part in ordinary temperature. In addition, gelation or the solidification agent of this invention may blend independent or the solid-state fat which becomes this from glycerides, such as other palmitic acids which are a candelilla wax, waxes, for example, carnauba wax, with conventionally still better known optimum dose, a montan wax, a micro crystallin wax, paraffin wax, etc., stearin acid, and behenic acid, unless it deviates from the purpose of this invention, although only mixture does not interfere of said esterification product. Moreover, you may use together with said well-known gelling agent.

[0016]

[Example] In the following synthetic examples and examples, % is weight criteria.

Glycerol 92g (1.0 mols), 569g (2.0 mols) of stearin acid, and 171g (0.5 mols) of eicosa dicarboxylic acid were taught to the 4 Thu openings flask furnished with synthetic example 1 agitator, a thermometer, gas blowing-in tubing, and a water separator, xylene 5% was added as 0.1% of p-toluenesulfonic acid, and a reflux solvent as a catalyst, and among the nitrogen gas air current, the esterification reaction was performed for 10 hours until the fall of the acid number was no longer accepted at 180-230 degrees C. Deodorization processing by decolorization and steam blowing in was performed by rinsing and activated carbon after reaction termination, and 663g (sample notation: referred to as A) of esterification products of this invention was obtained. this thing — acid-number: — they were 2.0, hydroxyl value:7.0, and melting point:58-60 degree C.

[0017] 17g (0.05 mols) of eicosa dicarboxylic acid was added to deca glycerol 75g (0.1 mols) of 10, and 170g (0.5 mols) of behenic acid, and synthetic example 2 average degree of polymerization performed the esterification reaction like the synthetic example 1, carried out purification processing, and obtained 201g (sample notation: referred to as B) of esterification products of this invention. this thing — acid-number: — they were 0.5, hydroxyl value:134, and melting point:52-57 degree C.

[0018] Tricaprilin 47g which esterified synthetic example 3 glycerol and the caprylic acid with the conventional method, and obtained them (0.1 mol), The approach of a Japanese Patent Application No. [for which these people applied previously / No. 230734 / five to] publication, i.e., the settlings of the Goma crude oil, (cage) is distributed to ethanol. Make it dissolve, and cool, and use 23g (0.05 mols) of OKUTAKOSA dicarboxylic acid obtained by separating the insoluble matter which deposits as a raw material, and lipase (the Meito Sangyo Co., Ltd. make, lipase QL) is added 1% of opposite raw materials. Stirring at 120 degrees C, the gas chromatography analyzed the content of the caprylic acid which carries out a byproduction, and the ester exchange reaction was performed for 72 hours until the increment was no longer accepted. The reactant was refined like the synthetic example 1 after reaction termination, and 59g (sample notation: referred to as C) of esterification products of this invention was obtained. this thing — acid-number: — they were 6.0, hydroxyl value:5.0, and melting point:58-64 degree C.

[0019] The synthetic example 4 (example 1 of comparison composition)

171g of eicosa dicarboxylic acid in the synthetic example 1 was replaced with 59g (0.5 mols) of succinic acids, it processed by the same approach, and the esterification product (sample notation: referred to as D) was obtained. this thing — acid-number: — they were 6.3, hydroxyl value:8.5, and melting point:53-56 degree C.

[0020] The gelation ability to the esterification product (sample notation: A-D) obtained in the examples 1-4 of example 1 composition, 12-hydroxy stearin acid, and the soybean oil of carnauba wax was examined. The result is shown in Table 1. In addition, after heating and fusing the examining method at 80 degrees C, taking and stirring soybean oil and 3% of each of its sample to a beaker and cooling radiationally in ordinary temperature as it is for 1 hour, the condition of the obtained gel object was observed. evaluation — O: — a hard, uniform, and smooth gel object and O: — a uniform and smooth gel object and **: — the part considered as what carries out solid liquid separation, and the thing of which x:solidification is not done.

[0021]

[Table 1]

表1 大豆油のゲル化又は固化物

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添加物	本 発 明 例			比 較 例		
	試料A	試料B	試料C	試料D	12-ヒドロキシステアリン酸	カルナウバワックス
固形物の状態	◎	◎	◎	×	◎	×

[0022] It became clear that it forms a uniform gel solidification object to soybean oil although the esterification product (sample notation: A-C) of Table 1 to this invention is little addition compared with a conventional gelling agent and a conventional wax. Moreover, when these were saved for one month in ordinary temperature, what added the esterification product of this invention was maintaining the homogeneity condition, and the stable thing was accepted. In addition, although 12-hydroxy stearin acid made soybean oil solidify, the solid was hard and it was very a BOSO ***** feel, and the original solid was not reproduced when this was ***** (ed) one time. On the other hand, the esterification product of this invention is very smooth, has viscosity nature, and even if it crushed this, it returned to the original gel state easily. Sample D was inferior in gelation ability.

[0023] The gelation or solidification ability to the various organic liquids of the esterification product (sample number: A) obtained in the example 1 of example 2 composition was investigated by the same approach as an example 1. The result is shown in Table 2. In addition, the sign of evaluation is the same criteria as an example 1. From Table 2, to various liquids, the esterification product of this invention was little, had solidification ability, moreover presented description with a viscous student uniform [a solid] and smooth, and found that this property was effective to the broad polar substance.

[0024]

[Table 2]

表2 各種有機液体のゲル化又は固化物

有 機 液 体	試料Aの添加率と固形物の状態	
	1 %	3 %
イソパラフィン	○	○
流動パラフィン	○	◎
イソノナン酸イソノニル	○	○
トリイソオクタン酸グリセリル	○	◎
リンゴ酸ジイソステアリル	○	◎
トリイソステアリン酸ジグセリル	○	◎
ジイソステアリン酸ジグセリル	○	◎
モノイソステアリン酸ジグセリル	○	◎
ヒマシ油	○	◎
大豆油	○	◎
オレイン酸	△	○
灯油	×	○
エタノール	×	×
n-ブタノール	×	○
1, 3-ブタンジオール	×	×

[0025] According to the approach of the example 1 of example 3 composition, various esterification products (sample notation: 1-12) were compounded, it added 3% to TORIISO octanoic-acid glyceryl, and gelation or solidification ability was investigated. The result is shown in Table 3. In addition, the sign of evaluation is the same criteria as an example 1. It became clear that desirable gelation or a solidification agent can be prepared by combining suitably a fatty acid, a dibasic acid, and polyhydric alcohol from Table 3. Moreover, when more than one half of the hydroxyl group was esterified also about polyglycerin, it was fully able to solidify.

[0026]

[Table 3]

表3 各種エステル化生成物のゲル化又は固化能

	試料 番号	エステル化生成物の原料（モル比）			固形化物 の状態
		脂肪酸 ¹⁾	二塩基酸 ¹⁾	アルコール	
本 発 明 例	1 ²⁾	C22（2.0）	C20（0.5）	グリセリン（1.0）	◎
	2 ³⁾	C22（5.0）	C20（0.5）	デカグリセリン(1.0)	○
	3 ⁴⁾	C 8（2.0）	C28（0.5）	グリセリン（1.0）	◎
	4	C 2（2.0）	C28（0.5）	グリセリン（1.0）	○
	5	C22（2.0）	C28（0.5）	グリセリン（1.0）	○
	6	C18（2.0）	C20（0.5）	グリセリン（1.0）	○
	7	C16（2.0）	C20（0.5）	グリセリン（1.0）	△
	8	C28（2.0）	C12（0.5）	グリセリン（1.0）	○
	9	C22（1.5）	C20（0.7）	グリセリン（1.0）	◎
比 較 例	10	C22（2.0）	C20（0.5）	TMP ⁶⁾ （1.0）	×
	11	C22（3.0）	C20（0.5）	PE ⁷⁾ （1.0）	×
	12 ⁵⁾	C18（2.0）	C 4（0.5）	グリセリン（1.0）	×

Note One carbon number was expressed as C numeric value. For example, as for C22 of a fatty acid, C20 of a HEBEN acid and a dibasic acid is eicosa dicarboxylic acid.

2) It is the same as the sample notation A.

3) It is the same as the sample notation B.

4) It is the same as the sample notation C.

5) It is the same as the sample notation D.

6) TMP:trimethylol propane 7PE : pentaerythritol [0027]

[Effect of the Invention] According to this invention, they are a glycerol or its condensate, and the straight chain-like saturated fatty acid of carbon numbers 2-28. An esterification product with the aliphatic series saturation dibasic acid of carbon numbers 12-28 is obtained, it is only carrying out little addition of this at the ester which presents the shape of liquid in ordinary temperature, fats and oils, hydrocarbons, a polarity, a nonpolar organic solvent, etc. (however, alcohol with a carbon numbers of four or more monohydric alcohol), and homogeneity and the stable gelation which is smooth and has viscosity nature, or a solidification object can be formed. Therefore, the esterification product of this invention can be made with the gelation or the solidification agent of an organic liquid which was excellent in the gelation ability of the low melting point compared with the conventional thing, and this gelation or a solidification agent can be effectively utilized as a solvent, the processing agent of oils, lubricant, a release agent, adhesives, a binder, a sealing agent, lubricant, the coating, a paint film agent, a volatile-component modifier, etc.

[Translation done.]

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